

ALLYL STARCH EMULSIONS¹

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The preparation, properties, and potential uses of allyl starch have been described in a number of publications³. The product is now undergoing commercial development as a resin of varied applications. It makes excellent printing inks of the steam-set and gravure types as well as aniline inks, being particularly useful in high-gloss inks for cellophane and glassine paper⁴. As a surface coating, it has attractive potentialities in furniture finishing and various other uses. As a uniform product made from non-critical domestic raw materials, allyl starch can compete with shellac in all its uses.

For most applications, solutions of allyl starch are used. For such applications as sizing of paper or textiles, water emulsions are preferable. Moreover, some industrial users prefer water emulsions of allyl starch to obviate fire hazards or the necessity of installing solvent recovery equipment. To be useful industrially, the emulsions should meet certain requirements—they should be easy to prepare, have reasonably good stability, and deposit clear films. Various methods for achieving this end are described here.

Preliminary Experiments

The first method of attack on the problem of emulsifying allyl starch was to grind the allyl starch solids with water and dispersing, emulsifying, and stabilizing agents for 60 hours in a ball mill, operated in a cold room to facilitate comminution. The reagents employed were anionic dispersing and emulsifying agents such as Alkanol S⁵, Duponol ME, Darvan No. 1, Triton 720; colloidal stabilizers such as Protovac 8979 or Ammonium Alginate; and ammonia.

Although the rather time-consuming milling process gave emulsions stable for more than a month, the air-dried films made from such emulsions were hazy. Addition of plasticizers before or during the ball milling interfered with the milling by making the solid material too gummy. For emulsification of plasticized allyl starch, a kneading machine operated at 90° C. for the blending of the resin with plasticizer and at 60° C. for the emulsification, worked better than ball milling, but yielded excessively viscous emulsions.

Plasticized allyl starch emulsions were also obtained by blending a separate plasticizer emulsion with an allyl starch emulsion. Such mixed emulsions of Flexol TWS and allyl starch deposited clear air-dried films, but had the disadvantage of relatively short shelf life.

Allyl Starch-Solvent-Plasticizer Emulsion

Following the principle that increasing the liquid character of the internal phase should increase the effectiveness of an emulsification process, solutions of plasticized allyl starch in toluene were emulsified with the help of Duponol ME and sulfonated castor oil, as recommended for nitrocellulose solutions⁶. Although water-in-oil emulsions resulted, the ease of preparation and the attainment of clear films suggested work along a similar line in which solution formation would be concurrent with a blending process.

To this end, moist commercial allyl starch solids (70% allyl starch, 30% water) were mechanically kneaded at 90° C. with Flexol TWS plasticizer and toluene-butanol (95:5), producing smooth pastes, of which aliquots could be taken for testing various emulsifiers. Tests on a number of substances indicated the suitability in this application of an alkylated aryl polyether alcohol emulsifier, Triton X-100. Favorable results were obtained with the formulations shown in Table I.

Table I.

Allyl Starch-Plasticizer-Solvent Emulsions			
Formulation No.	1	2	3
Allyl starch, g.....	60	60	72
Flexol TWS, g.....	20	6.7	8
Toluene-butanol, g....	20	33.3	20
Triton X-100, g.....	5	5	5
Water, g.	40	40	50

To supply the indicated dry-basis weights of allyl starch, higher amounts of 70 per cent solid moist resin were employed, and correspondingly lower weights of water were added at the end of the process. It was found that allyl starch could be blended with plasticizer and solvent either in an efficient mechanical kneader or simply in a three-necked laboratory flask fitted with wire stirrer and condenser.

In typical experiments with laboratory glassware, the Triton X-100 was stirred into the wet resin-plasticizer-solvent blend at 90° C. After bringing the resulting viscous water-in-oil emulsion down to room temperature, additional water was gradually added, with continued agitation, to somewhat beyond the inversion point. Fluid oil-in-water emulsions giving clear air-dried films were obtained; the films from the first formulation were rather soft, but those from formulations 2 and 3 were moderately hard.

Allyl Starch-Plasticizer Emulsions

The emulsions described above (Table I) were satisfactory, but they still called for considerable amounts of volatile organic solvent. Since reduction in the solvent content beyond that indi-

cated in the third recipe gave poor results, an auxiliary emulsifier was sought. After a number of auxiliary agents were tested in a formulation including 20 per cent of plasticizer and 5 per cent of Triton X-100, concentrated ammonia was found effective. Table II shows two formulations so developed, which give rise to a new series of emulsions.

Table II. Allyl Starch-Plasticizer Emulsions

Formulation No.	1	2
Allyl Starch, g.....	80	85
Flexol TWS, g.....	20	15
Triton X-100, g.....	5	5
NH ₄ OH, conc., ml....	1-3	2
Water, total, g.....	100-170	100-170

The laboratory-scale preparation of these emulsions is conveniently carried out in a 500-ml. three-necked flask equipped with wire stirrer, reflux condenser, and a system for maintaining a nitrogen atmosphere. A stirring motor having two or three gear ratios is useful for this work. Enough allyl starch solids of 30 per cent water content to afford the indicated quantities of dry-basis resin is ground with a mortar and pestle and charged to the flask. After the plasticizer has been stirred in and a nitrogen atmosphere established, the flask is set in a 90° C. bath, where blending of the allyl starch and plasticizer is continued for one hour. The emulsifier and ammonia are then added, and the mixture is stirred for 15 minutes. Finally the flask is transferred to a cooler bath—25, 40, or 60° C.—and water is slowly added from a dropping funnel in accordance with the inversion technique, finishing as an oil-in-water emulsion. Allowance is made for the water content of the allyl starch solids used. The viscosity of the blend of allyl starch, plasticizer, and emulsifiers governs the temperature of the bath during the addition of water. Forty degrees centigrade is most generally satisfactory.

Since different batches of the allyl starch may vary slightly in substitution, molecular weight, and acidity, small variations in formulation or technique are sometimes necessary. Since a final pH of 8 to 10 is most satisfactory, some batches require the use of 2 or 3 ml. of concentrated ammonia instead of one. With some batches, the minimum water content of the finished emulsion must be 130, 150, or 170 grams instead of 100. With the higher contents of water, addition of a dispersing agent—Alkanol S, for example—gives smoother films.

Emulsions of this type are generally stable for 6 months or more. They yield clear, glossy films by either air-drying or baking.

The size of the emulsion droplets is generally small, 0.5 to 3 microns, with much Brownian movement evident. In general, viscosities range from 20 to 200 centipoises. In view of the tolerance to dilution, however, it is possible to get extremely dilute and fluid emulsions if desired. For instance, emulsion 1 of Table II, with 700 g. of water, had a viscosity of 3 centipoises.

To cure films cast from the emul-

perature may be employed. Baking at 150° C. for 20 or 30 minutes gives hard films. At room temperature, although the films dry to the touch in 20 to 30 minutes, they remain soft and easily marred for a week or more because of the high content of soft plasticizers. This can be partly offset by reducing the proportion of plasticizer. Good emulsions can be made with as little as 10 per cent Flexol TWS; and if the Triton X-100 is increased to 10 per cent the plasticizer can be omitted entirely. This seems to be possible because of some plasticizing action exerted by the emulsifier itself.

Another approach to the problem of softness of the films is the use of other plasticizers. A series using from 20 to 10 per cent of Aroclor 1242 can be made with the same emulsifiers and by the same method. Somewhat firmer films are obtained, but on close examination the films often show microbubbles.

At the suggestion of Robert Nordgren of General Mills, Inc., plasticizers derived from castor oil have also been incorporated in such emulsions. A series of this kind was based on P-10 Plasticizer. An example is the formulation: 95 g. allyl starch, 5 g. P-10, 10 g. Triton X-100, 1.1 g. morpholine, 1 g. Alkanol S, 150 g. water. Clear, smooth, rather soft films were obtained from this emulsion.

Another series of emulsions was based on glycerol monoricinoleate as plasticizer. Emulsions of good clarity were made from both a soap-containing or emulsifiable grade, (Glycerol Monoricinoleate S), and a soap-free grade (Glycerol Monoricinoleate S-1153). Formulations in this series involved allyl starch, plasticized with 5 to 20 per cent (with optimum at about 10 per cent) of one of the monoester preparations. To each 100 g. of plasticized allyl starch, 5 g. Triton X-100, 1 g. Alkanol S, 1 ml. ammonium hydroxide, and 175 ml. water were added. Fine droplet size and satisfactory stability characterized these emulsions.

Omission of Protection from the Air

In most of our emulsification experiments, an atmosphere of nitrogen has been maintained to protect the allyl starch from oxidation, particularly during heating at 90° C. Since in some plants provision of such protection might be inconvenient, the effect of blending and emulsifying without a nitrogen atmosphere was tested. In the series utilizing Flexol TWS as plasticizer, the nitrogen blanket was omitted with little ill effect, provided Alkanol S was not used. If Alkanol S was used, the emulsions rapidly increased in viscosity on storage for a few days. In the Aroclor 1242 series, this effect was not evident. It was also possible to obtain stable emulsions in the glycerol monoricinoleate series without the protection of an inert gas. In all series, however, filtration must then be more thorough to obtain smooth films.

Emulsifiable Pastes

In shipping allyl starch solids con-

usually done under additional water to protect the resin from oxidation, or in shipping allyl starch emulsions themselves, a considerable portion of the freight charge is due to the water. This expense could be reduced by using an emulsifiable paste, which could be converted by the consignee into emulsions as required.

Experiments have indicated that preparation of such pastes and their emulsification at a later date are feasible.

Thus half a kilogram of paste was made of the following composition:

Allyl starch, 71.4% solid...	119 parts
(containing on dry basis) (85) "	
Aroclor 1242	15 "
Triton X-100	5 "
Alkanol S	1 "
	140

The allyl starch and Aroclor plasticizer were kneaded mechanically for 15 minutes at 90° C. without exclusion of air; then the Triton X-100 and Alkanol S were added and blended in for 15 minutes more. The paste was cooled by circulating cold water through the jacket of the kneading machine, and was then transferred to a mason jar. A few milliliters of water from the lid and condenser of the machine partially covered the paste. The half-filled jar was stored on a shelf under normal conditions of diffuse interior light for one month. The paste contained 25 per cent moisture, due to the water content of the original allyl starch. But if dry solids were used, the water content would be negligible. Except for the formation of a whitish crust on top, the paste appeared unchanged after the storage period.

Tests on aliquots of the paste indicated the practicality of the following method of emulsification: After 140 g. of the paste are briefly stirred at 90° C., 2 ml. of concentrated ammonium hydroxide are added and mixed in over a period of 15 minutes. The flask is then transferred to a 40° C. bath, and with continued stirring, enough water is slowly added to bring the total water content to 170 grams. Finally the flask is removed from the bath, and the contents are allowed to cool slowly to room temperature. The resulting emulsions are comparable with those made at one time. Similar results were obtained after four months' storage.

Pigmented Emulsions

The incorporation of pigments in allyl starch emulsions is under investigation, and an emulsion pigmented with titanium dioxide may be reported at this time. For the preliminary preparation of a pigment dispersion, 200 g. of fine titanium dioxide was ball-milled for 11 hours with 1 g. of Triton X-100, 1 ml. of concentrated ammonia, and 200 g. of water.

Now 85 g. of allyl starch (on the dry basis) were blended at 90° C. in a nitrogen atmosphere with 15 g. of Flexol TWS. After 35 minutes, 5 g. of Triton X-100 and 2 ml. of concen-

mixed in. After 7 minutes more, with the bath still at 90° C., 34 grams of the previously prepared pigment dispersion (17 g. of titanium dioxide) were slowly added through a dropping funnel. At the end of 23 minutes, when the pigment had all been added, the flask was transferred to a 40° C. bath, where sufficient water to bring the water content up to 170 grams was slowly added. The cooled emulsion was filtered through glass wool.

The resulting enamel had a viscosity of 48 centipoises. It deposited smooth, glossy air-dried films. The films dried hard in 3 days instead of a week, the usual time required without the pigment. Although the pigment settled from the emulsion in a few days, the emulsion itself was stable, and the pigment could readily be redispersed by shaking.

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³a) Nichols, P. L., Jr., Hamilton, R. M., Smith, L. T., and Yanovsky, E., Allyl Ether of Starch, Preparation and Industrial Possibilities: *Ind. Eng. Chem.*, **37**, 201-202 (1945).

b) Talley, E. A., Hamilton, R. M., Schwartz, J. H., Brown, C. A., and Yanovsky, E., Preparation of Allyl Starch: U. S. Dept. of Agr., Bureau of Agricultural and Industrial Chemistry, AIC-140 (Eastern Regional Research Laboratory), February 1947. (Processed.)

c) Dietz, T. J., Hansen, J. E., and Gallagher, M. E., Properties of Allyl Starch Coatings: U. S. Dept. of Agr., Bureau of Agricultural and Industrial Chemistry, AIC-175 (Eastern Regional Research Laboratory), February 1948. (Processed.)

d) Roach, J. R., and Nordgren, R., Allyl Starch—A New Chemurgic Resin, *Organic Finishing*, April 1950, p. 8, 13, 15.

e) Nordgren, R., Baker, M. H., Champlin, L., Jr., Allyl Starch: Paint, Oil and Chem. Rev., January 18, 1951, p. 15-16, 36, 38.

f) General Mills, Inc., Allyl Starch, New Product Data Sheet R, April 5, 1951.

Anonymous, Allyl Starch, A New Raw Material for the Printing Ink Industry: *American Ink Maker*, **28**, 27, 59, 61, 63 (May 1950).

The mention of commercial products in this paper does not indicate that they are endorsed or recommended by the Department of Agriculture over similar products not mentioned.

Bennett, H., *Practical Emulsions* (Chemical Publishing Co., Inc., Brooklyn, 1943), p. 318, Formula No. 11.

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